REMARKS

(A) STATUS OF THE APPLICATION

Applicants thank the Examiner for his extensive explanation for withdrawing the previous rejections in the Office Action dated September 27, 2005.

Applicants also agree with his interpretation of the phrase "has little or no tendency to copolymerize ethylene and α-olefins".

DISPOSITION OF CLAIMS

(i)   Claims 26-28, 30-33 and 35-39 are pending in the application.

(ii)   Claims 26-28, 30-33 and 35-39 have been rejected under 35 U.S.C. § 112, first paragraph.

(B) RESPONSE TO REJECTION UNDER 35 U.S.C. § 112

Claims 26-28, 30-33 and 35-39 have been rejected under 35 U.S.C. § 112, first paragraph, for failing to enable the invention. Specifically the Examiner points to the idea that Ziegler-Natta (ZN) and metallocene catalysts may all copolymerize ethylene and α-olefin well and/or similarly.

Applicants respectfully point out that it is known in the art that not all ZN and metallocene catalysts are good for this copolymerization. The more well known and/or most used ZN and metallocene catalysts tend to be good for this copolymerization since often the copolymer is the desired product. We draw the attention of the Examiner to the quote that he has cited from page 13 of the specification and respectfully point out that the quote does not state that all ZN and metallocene catalysts are good copolymerization catalysts. It states that such catalysts include ZN-type and metallocene catalysts.

Applicants enclose herewith relevant parts of a review paper addressing this issue. The review article is H.H. Brintzinger, et al., Angew. Chem. Int. Ed. Engl, 1995, vol. 34, p. 1143-1170.

Pages 1158-1159 of the review article discuss such copolymerizations using ZN and metallocene catalysts. The article clearly shows that there are metallocene and ZN catalysts, which are significantly poorer at copolymerizing ethylene and α-

olefins when compared to other ZN and metallocene catalysts. For instance, Table 1 on p. 1159 gives copolymerization parameter r_1 and r_2 for such copolymerization for a variety of catalysts. When r_2 is low relative to r_1 the, copolymerization of the α-olefin is quite low compared to the polymerization uptake of ethylene. This is clearly the case with many of catalysts in Table 1. This table, and the text on these two pages clearly show that in 1995, well before the filing date of the present case (2003), it was known that some ZN and metallocene catalysts were relatively poor at incorporating α-olefins.

Applicants also respectfully point out that since this is a review article and not an obscure research paper, a person of ordinary skill in the art of olefin polymerization would be aware of the above technology. Since "[t]he disclosure of an application embraces not only what is expressly set forth in words or drawings, but what would be understood by persons skilled in the art; . . ." *Ex parte Wolters, et al.,* 214 USPQ 735,(POBA 1979), these claim are enabled and this rejection is overcome.
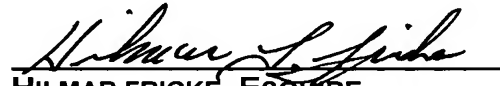
CONCLUSION

In view of the above remarks, Applicants respectfully submit that stated grounds of rejection have been properly traversed, accommodated, or rendered moot and that a complete response has been made to the Office Action mailed on September, 2005.

Therefore, Applicants believe that the application stands in condition for allowance with withdrawal of all grounds of rejection. A Notice of Allowance is respectfully solicited. If the Examiner has questions regarding the application or the contents of this response, the Examiner is invited to contact the undersigned at the number provided.

Should there be a fee due which is not accounted for, please charge such fee to Deposit Account No. 04-1928.

Respectfully Submitted,

DATED: _December 9, 2005_   _____

HILMAR FRICKE, ESQUIRE
ATTORNEY FOR APPLICANTS
REGISTRATION NO.: 22,384
PHONE: 302-984-6058
FAX: 302-658-1192

Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts

Hans H. Brintzinger,* David Fischer, Rolf Mülhaupt, Bernhard Rieger, and Robert M. Waymouth

Dedicated to all those excellent graduate students who are the true heroes of this story

Current studies on novel, metallocene-based catalysts for the polymerization of α-olefins have far-reaching implications for the development of new materials as well as for the understanding of basic reaction mechanisms responsible for the growth of a polymer chain at a catalyst center and the control of its stereoregularity. In contrast to heterogeneous Ziegler–Natta catalysts, polymerization by a homogeneous, metallocene-based catalyst occurs principally at a single type of metal center with a defined coordination environment. This makes it possible to correlate metallocene structures with polymer properties such as molecular weight, stereochemical microstructure, crystallization behavior, and mechanical properties. Homogeneous catalyst systems now afford efficient control of regio- and stereoregularities, molecular weights and molecular weight distributions, and comonomer incorporation. By providing a means for the homo- and copolymerization of cyclic olefins, the cyclopolymerization of dienes, and access even to functionalized polyolefins, these catalysts greatly expand the range and versatility of technically feasible types of polyolefin materials.

Keywords: alkenes · catalysis · metallocenes · polymerizations
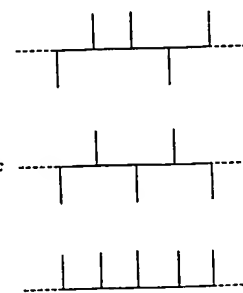
1. Introduction

Forty years after Karl Ziegler's invention of transition metal catalyzed polyinsertion and Giulio Natta's discovery of the stereoselective polymerization of α-olefins,[1–4] we are witnessing the evolution of new generations of catalysts and polyolefin materials, which originate from studies on homogeneous, metallocene-based polymerization catalysts. In the following, we will attempt to review some of these recent developments.[5–7]

Research on metallocene-catalyzed olefin polymerization has derived much of its impetus from the desire to model the reaction mechanisms of heterogeneous polymerization catalysts. In the evolution of Ziegler–Natta catalysis, an empirical approach has proven highly successful. Modern $MgCl_2$-supported catalysts have tremendous activities for the production of polypropene and other polyolefins; at the same time, they are
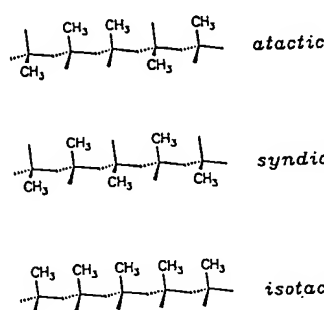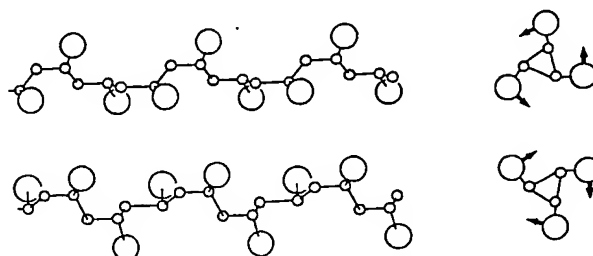

Scheme 1. Structure of isotactic, syndiotactic, and atactic polypropene in sawhorse and modified Fischer projections [107] (top), and conformation of the chains in crystalline isotactic polypropene, determined by Natta and Corradini [2] (bottom).

[*] Prof. Dr. H. H. Brintzinger
    Fakultät für Chemie der Universität
    D-78434 Konstanz (Germany)
    Telefax: Int. code +(7531) 883137

    Dr. D. Fischer
    BASF AG, Abteilung ZKP
    Ludwigshafen (Germany)

    Prof. Dr. R. Mülhaupt
    Institut für Makromolekulare Chemie der Universität Freiburg (Germany)

    Dr. B. Rieger
    Institut für Anorganische Chemie der Universität Tübingen (Germany)

    Prof. Dr. R. M. Waymouth
    Department of Chemistry, Stanford University (USA)

in Sections 4.1 and 4.2, respectively. Development of truly living α-olefin polymerization systems remains a challenge.[162]

Stereoregularity, regioregularity, and chain length of a polypropene all appear to influence its crystallinity as well as its melting behavior and mechanical properties. Heterogeneously produced isotactic polypropenes normally crystallize in a regular packing of parallel helices, the classical α-modification.[163] In contrast, isotactic polypropenes produced by homogeneous, C_2-symmetric *ansa*-zirconocene catalysts often crystallize from their melts with sizeable fractions of a heretofore infrequently observed[164] γ-modification,[114, 165–167b] which was found by Brückner and co-workers to contain alternate layers of helices oriented at an angle of 81° to each other.[166] For a given polypropene sample, the fraction of this γ-modification, as measured by wide-angle X-ray diffraction (WAXD), appears to be inversely related to the average length of isotactic chain segments, n_{iso}, if one takes into account that stereoerrors as well as regioinversions and chain ends limit the length of the isotactic segments.[69b, d, 168]

Statistical factor analysis has been used to correlate the melting points of isotactic polypropenes with the substituent patterns of the *ansa*-zirconocene catalysts used, without differentiating between effects of regio- and stereoerrors and chain lengths variation.[169a] Melting points and total crystallinity both appear to be directly correlated with the average length of isotactic chain segments in these polyolefins.[69d] A finite fraction of noncrystalline segments within each polypropene chain appears to augment the toughness of the polymer materials.[117c, 169b] These segments apparently function as flexible links between the crystalline polymer domains (Fig. 7).
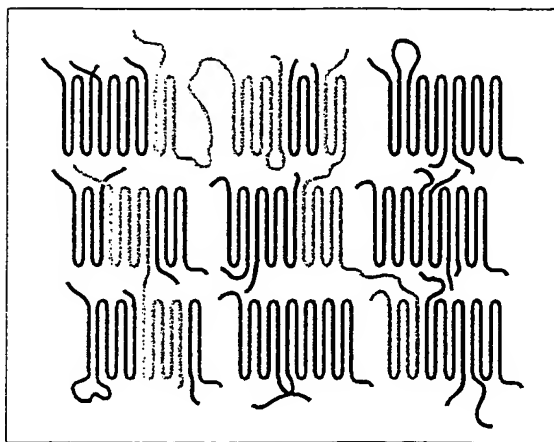

Fig. 7. Noncrystalline segments within longer polymer chains act as flexible links; they connect the crystalline polymer domains and render the polymer tougher (less brittle).

Several crystal modifications have now also been characterized for the syndiotactic polypropenes formed with C_2-symmetric metallocene catalysts.[167c, 170–173] Their crystallinity appears to correlate again with the length of uninterrupted syndiotactic chain segments;[174] a large proportion of an amorphous phase, together with a small crystallite size, appears to cause the high transparency of this material.[169b] Syndiotactic polypropene can slowly form highly crystalline solids with a melting point of about 160 °C when kept just slightly below the melting temperature.[171b] Correlations between the structures of polyolefin materials produced with different homogeneous catalysts and their respective thermal, mechanical, and optical properties are presently being studied in more detail than can be accounted for within the limits of this review.[167, 175]

4. Olefin Copolymerization and New Polyolefin Materials

While the development of homogeneous, chiral metallocene catalysts can be seen mainly as an opportunity for in-depth studies on the fundamental principles of stereoselective α-olefin polymerizations, two examples of homogeneously produced polymers encountered already, syndiotactic and hemiisotactic polyolefins, are inaccessible with heterogeneous Ziegler–Natta catalysts. In the following chapter, we summarize additional examples for the formation of polyolefin materials by homogeneous metallocene catalysts which extend beyond the capabilities of classical heterogeneous polymerization catalysts.

4.1. Copolymers from Ethene and Higher Olefins

Olefin copolymers, especially those of ethene with propene and/or another α-olefin, are of great practical interest; their total production volume is comparable to that of the homopolymers. New possibilities for controlling the properties of olefin copolymers with metallocene-based catalysts have recently caught the interest of industrial chemists and will thus be summarized here.

Linear polyethene with short-chain branches, which has low crystallinity and, hence, low density (*linear low-density polyethene*, LLDPE) is obtained by copolymerization of ethene with 1-butene, 1-hexene, and/or 1-octene.[176] Its mechanical properties, which differ from those of the long-chain branched LDPE (*low-density polyethene*) produced by high-pressure radical polymerization, make LLDPE one of the largest volume polyolefin products. Copolymerization of propene with small amounts of ethene gives copolymers of lower crystallinity;[177] increased fractions of ethene lead to amorphous materials with rubber-like elasticity (EP-rubbers). Blending of these EP-rubbers with the stiffer but brittle polypropene yields heterophase materials with balanced toughness–stiffness properties which have opened new ranges of practical applications for these polyolefin blends.[178, 179]

Mechanical, thermal, and optical properties of these copolymers obviously depend on their comonomer content; however, to a significant degree they also depend on the distribution of the comonomers between and within individual polymer chains. If a catalyst distributes the comonomers randomly along each chain, an amorphous polymer is to be expected, whereas partially crystalline polymers are likely to result when the monomers are collected into separate blocks.

The comonomer selectivity of a given catalyst, in other words its tendency to insert one of two competing monomers into each type of metal–chain-end bonds, is expressed by its copolymerization parameters r_1 and r_2 (the subscripts specify the monomer).[176a, 180] These are defined as $r_i = k_{ii}/k_{ij}$, the ratio of

1158

the rate constant for a homopolymerization step (k_{ii}) over that for a copolymerization step (k_{ij}).[181, 182] The product $r_1 r_2$ is an indicator for the distribution of two monomers along each chain.[170] Values of $r_1 r_2 > 1$ indicate that a catalyst tends to collect at least one of the comonomers into separate blocks, while a catalyst with $r_1 r_2 < 1$ tends to alternate isolated comonomer units along each chain.[183]

Values of $r_1 r_2 > 1$ are typical for ethene–propene copolymers made with heterogeneous polymerization catalysts[177b, 184b] (Table 1) and indicate that these catalysts tend to collect each

Table 1. Copolymerization parameters r_1 and r_2 for ethene and a second α-olefin. For heterogeneous catalysts (entries 1–3) values of $r_1 r_2 > 1$ indicate that the monomers are incorporated in blocks; for metallocene-based catalyst systems (entries 4–9), random or alternating monomer sequences are indicated by values of $r_1 r_2 \leq 1$.

Entry	Catalyst	r_1	r_2	$r_1 r_2$
1	δ-TiCl$_3$/AlEt$_3$ [176c]	7.3	0.76 [a]	5.5
2	MgCl$_2$/TiCl$_4$/AlEt$_3$ [184a]	–	– [a]	4
3	SiO$_2$/MgCl$_2$/TiCl$_4$ AlEt$_3$ [184a]	5–10	0.2–0.34 [a]	1.9
4	(C$_5$H$_5$)$_2$ZrCl$_2$/MAO [190]	48	0.015 [a]	0.72
5	C$_2$H$_4$(ind)$_2$ZrCl$_2$/MAO [194a]	2.57	0.39 [a]	1.0
6	C$_2$H$_4$(thind)$_2$ZrCl$_2$ MAO [194a]	2.90	0.28 [a]	0.81
7	Me$_2$C(Cp)(flu)ZrCl$_2$ MAO [197]	1.3	0.20 [a]	0.26
8	C$_2$H$_4$(thind)$_2$ZrCl$_2$ MAO [193]	59	0.012 [b]	0.71
9	Me$_2$Si(ind)$_2$ZrCl$_2$ MAO [193]	25	0.016 [b]	0.4

[a] Ethene, propene. [b] Ethene/1-hexene.

Fig. 8. Holtrup cross-fractionation of a conventional (top) and a metallocene-derived (bottom) ethene–butene random copolymer (LLDPE). Whereas LLDPE produced by classical heterogeneous catalysts contains a mixture of polymer chains with different composition and chain lengths, LLDPE produced by metallocene catalysts shows chemical uniformity and a very narrow molecular weight distribution.

type of monomer into separate blocks. In addition, the nonuniform centers of heterogeneous polymerization catalysts have in general different copolymerization characteristics.[6, 176b, 185] Analysis of the copolymer products by *temperature-rising elution/fractionation* (TREF) and cross-fractionation[186] (Fig. 8) shows that the higher α-olefin is preferentially incorporated at the centers that produce shorter chains; higher olefins are thus enriched in the low molecular weight fractions of these copolymers.[187] This increases the content of extractables and tends to make these materials sticky, two generally undesirable properties.

In their early studies on chiral, metallocene-based catalysts such as (en)(thind)$_2$ZrCl$_2$/MAO, Kaminsky and co-workers had noticed that these catalysts polymerize propene or 1-butene with only modestly lower rates than ethene.[39c–h, 188] Accordingly, copolymers obtained with these catalysts contain larger fractions of higher olefins than those obtained with heterogeneous catalysts under comparable conditions.[176, 177] These and additional studies,[189–193] particularly by the groups of Zambelli,[122, 136b] Chien,[194] Soga,[195] and Kashiwa,[66, 97] showed that copolymers produced by metallocene-based catalysts consist of uniform chains with narrow molecular weight distributions typical of single-site catalysts. The copolymer chains contain the comonomers in nearly random placement,[196] as indicated by copolymerization-factor products of $r_1 r_2 \approx 1$ (Table 1); their TREF characteristics (Fig. 8) show that comonomer distributions are essentially independent of chain lengths, an important aspect for applications of these copolymers, for instance in films or sealant layers.

The copolymerization characteristics of metallocene-based catalysts vary with the metallocene complex used.[197] Higher
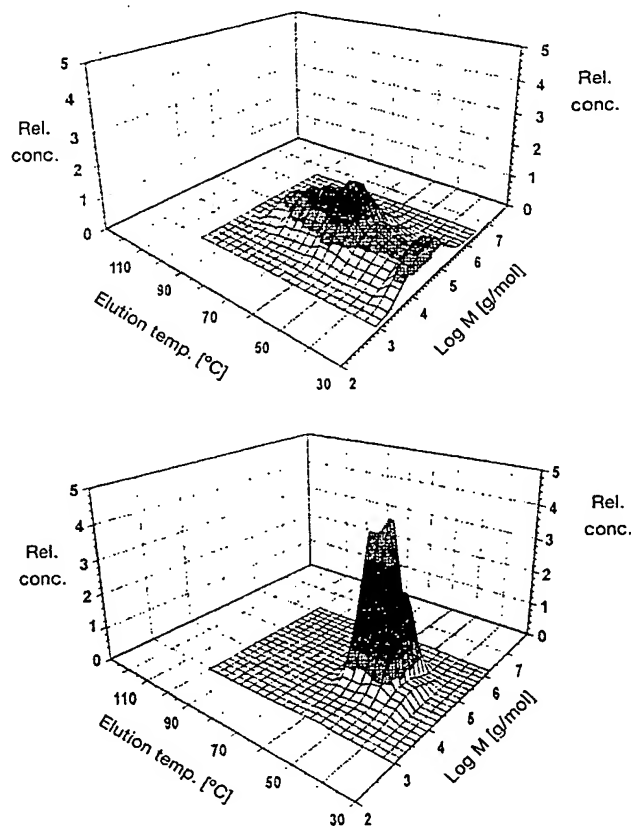
α-olefins are taken up more readily by isospecific, chiral *ansa*-metallocenes than by unbridged complexes. An even greater tendency for the incorporation of higher α-olefins is evident for the syndiospecific catalyst Me$_2$C(Cp)(fluorenyl)ZrCl$_2$/MAO. This trend reflects the rising activities in this series of catalysts for the homopolymerization of higher α-olefins as compared to that of ethene.[132a] But even monomers that are not homopolymerized by metallocene catalysts, for example isobutene,[188f] styrene, and 1,3-dienes,[188e, 191] are incorporated, albeit in minor amounts, into various copolymers.[39c, 188, 189d, 191, 194d]

Even less restricted than the metallocene-based catalysts with regard to comonomer selection are monocyclopentadienyl complexes such as MAO-activated dimethylsilyl-bridged amidocyclopentadienyltitanium complexes.[7a, 189c, 198] These catalysts (Fig. 9) incorporate into their polymer products even the vinylic end groups of polymer chains terminated by β-hydrogen transfer; they can thus generate copolymers with long-chain branches, in contrast to the strictly linear LLDPE copolymers produced by metallocene-based catalysts.[189c, 198a] These catalysts can also copolymerize styrene with ethene;[7a] styrene units in these copolymers are mostly isolated and of low regioregularity. Whether styrene–ethene and styrene–1,3-diene copolymers can be obtained also with the unbridged titanium system CpTiCl$_3$/MAO,[199–201] which catalyzes the syndiotactic homopolymerization of styrene,[7b] needs further clarification.[202]